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Blends of Natural and Synthetic Polymers

Agnieszka Wojtowicz, Leon P.B.M. Janssen, Leszek Moscicki

2.1

Introduction

In recent times, biodegradable materials have been growing in importance, particularly for the protection of the environment from ever-increasing plastic waste. The use of partially biodegradable polymers obtained through the blending of biodegradable and non-biodegradable commercial polymers can effectively reduce the volume of plastic waste thanks to partial degradation. The reasoning behind the approach for blends of starchy biodegradable polymers with inert polymers, such as PE, is that if the biodegradable component is present in sufficient amounts, and if it is removed by microorganisms in the waste disposal environment, the plastic or film containing the remaining inert components should then disintegrate and disappear.

The biodegradable products market and its perspectives are closely monitored by the different groups involved. According to a new technical market research report from BCC Research [1], the global market for biodegradable polymers reached 245 million kg in 2007. This market is expected to increase to over 545 million kg by 2012, with a compound average annual growth rate (CAGR) of 17.3%. The report breaks the market down into the separate applications of compost bags, loose-fill packaging, and other packaging, including medical/hygiene products, agricultural, and paper coatings and miscellaneous (Table 2.1). Currently the compost bags have the largest share of the market. At nearly 110 million kg in 2007, this segment is expected to reach 266 million kg by 2012, with a CAGR of 19.4%. Loose-filled packaging has the second largest share of the market, with production estimated at 73 million kg in 2007 and set to reach 97 million kg by 2012. The third largest segment, other packaging, is currently a 37 million kg segment predicted to reach 105 million kg by 2012, for a CAGR of 23.4%. BCC Research explains that growth rates are very high because the base volumes of biodegradable polymers are still relatively low in comparison with petrochemical-based polymers.

The loose-fill packaging growth rate is mainly attributable to two factors: lack of an effective infrastructure for disposal, and the popularity of air-filled plastics and

Table 2.1 Global biodegradable polymer market by application—million kg (million lbs.)[1].

Application	2006	2007	2012	CAGR% (2007–2012)
Compost Bags	78 (173)	110 (242)	266 (586)	19.4
Loose-Fill Packaging	69 (152)	73 (162)	97 (214)	5.7
Other Packaging ^a	23 (51)	37 (81)	105 (232)	23.4
Miscellaneous ^b	15 (33)	25 (56)	78 (171)	25.0
Total	186 (409)	245 (541)	545 (1203)	17.3

^a Includes medical/hygiene products, agricultural, paper coatings, etc.

^b Unidentified biodegradable polymers.

other materials for packaging. The biodegradable polymer market, although commercial for over 20 years, is still at a very early stage in its product life cycle. This market still has several major problems, the most important of which are relatively high prices and lack of an infrastructure for effective composting—an extremely critical aspect for biodegradable polymer market success. The North American biodegradable polymer market has not progressed as rapidly as in Europe and Asia, but is now beginning to show its potential. Major drivers for the U.S. market would be mandated legislation and prospective increases in landfill pricing—none of which are foreseen within the next five years, although recent increases in petroleum-based plastics have rekindled interest in biodegradable polymers.

2.2

Starch in Blends with Polymers

There exist an important number of biodegradable polymers (biopolymers) that are derived from both synthetic and natural sources. The utilization of agricultural products in plastic applications is considered an interesting way to reduce surplus farm products and to develop non-food applications.

Thermoplastic starch (TPS) or plasticized starch (PLS) is processed, like synthetic plastics, through extrusion and injection units [2]. Unfortunately, TPS is a very hydrophilic product, and additional processing of starch to reduce the hydrophilic character of the starch chains is sometimes necessary. There are some strict limitations to the development of starch-based products, due to its poor mechanical properties and high sensitivity to moisture. Starch is a very common, environmentally friendly, biopolymer. Raw, granular starch comes from a variety of sources, including corn, wheat, rice, and potatoes; wheat and rice granular starch tends to be the least expensive. However, pure starch is brittle and rapidly degrades when exposed to water. In efforts to overcome this disadvantage, there have been many attempts to combine starch with synthetic polymers. If starch were used as an additive in blends with polymers, it should not only increase their

biodegradability, but should also make them less expensive to synthesize. Mixtures of starch and polymers have resulted, however, in materials with poor physical qualities. The starch generally does not mix well with the polymers. In attempts to improve the mixtures, some researchers have used high-amylose starch [3]. Although high-amylose starch slightly improves the physical properties of the mixtures, it is relatively expensive and so reduces or eliminates the cost benefits of these mixtures. Gelatinized starch obtained from processing of raw starch has also been used in attempts to improve these mixtures. However, both gelatinized starch and high-amylose starch require the addition of a plasticizer (e.g., glycerol), and this poses another disadvantage: as well as requiring processing of the starch, it increases the cost. In addition, plasticizers such as glycerol increase the water absorption of polymer/starch mixtures. The addition of glycerol (plasticizer) not only damages the mechanical properties of starch-filled PE but also has a negative effect on the mechanical properties of starch-filled PE after storage, because glycerol is not compatible with PE.

Starch and more hydrophobic compounds such as biodegradable polyester are rather immiscible, and mixing produces blends with separated phases with poor interfacial properties. One strategy to overcome these weaknesses is to associate the starch with a moisture-resistant polymer with good mechanical properties, while maintaining the overall biodegradability of the product. Moisture sensitivity and critical aging have led to the necessity to associate TPS with other biopolymers, to preserve the biodegradabilities of the final blends. Association between polymers can be in the form either of blends or of multilayer products. Multilayers can be obtained by coating or by coextrusion processes; multilayer coextrusion has been widely used in the past decades to combine the properties of two or more polymers into one single multilayered structure. The preparation of starch-based multilayers may also be carried out through compression molding of plasticized starch and polyesters. These considerable research efforts have led to starch-based blends being commercialized, by Mater-Bi from Novamont (Italy) or by Bioplast from Biotec (Germany) [2]. To produce these commercial starch blends, starch can be blended either with non-biodegradable polymers (polyolefins) or with biodegradable polyesters (e.g., PCL). Applications involve packaging, disposable cutlery, gardening, leisure, hygiene, and the like.

Most research is focused on the blending of PLS with biodegradable polyesters: PCL (polycaprolactone), PEA (polyesteramide), PHBV (polyhydroxybutyrate co-hydroxyvalerates), PHBO (polyhydroxybutyrate co-hydroxyoctonate), PBSA (poly(butylene succinate/adipate)), PBAT (poly(butylene adipateco-terephthalate)), PLA (poly(lactic acid)), or PHEE (poly(hydroxy ester ether)) [3–5]. These commercially available polyesters show some interesting and reproducible properties, such as more hydrophobic characters, lower water permeabilities, and some improved mechanical properties, relative to PLS. The preparation of the blends is the main factor affecting their properties and their behavior during processing. The solid-state properties of the blends depend on the nature of the polyester phase. At ambient temperature, polyesters can be rigid (e.g., PLA) or soft (e.g., PCL, PBSA, PBAT), so the corresponding mechanical properties are tunable. Research results

have shown that PEA presents the highest surface tension, because of the highly polar component, and PLA the lowest. These different determinations allow the establishment of a classification from the least compatible (PLA) to the most compatible polyesters (PEA). However, low compatibility induces special behavior and properties: during the injection molding process, a preferential migration of the polyester, the low-viscosity polymer, toward the mold surface was observed. After cooling, a polyester-rich skin and a starchy core can be obtained.

PLS has been widely used in blends with other polymers, and a lot of patents have been published on this topic. This stratified pseudo-multilayer structure gives the blend rather good water resistance, in comparison with PLS itself, due to the polyester surface protection. Water sensitivity, determined by contact angle measurements with water drops, decreases drastically for polyester contents lower than 10% in the blend. The biodegradabilities of such blends are modified, with degradation occurring from the starchy core toward the skin.

A provisional patent application proposed by Wang *et al.* [6] presents biodegradable materials from starch-grafted polymers cross-reference to related applications. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polybutylene (PB), poly(styrene-ethylene-butylene styrene) (SEBS), polyvinyl fluoride (PVF), polyvinyl chloride (PVC), and poly(ethylene terephthalate) (PET) are some of the more common plastics. They are non-biodegradable and are generally synthesized from petroleum products. Several alternative materials to replace these plastic polymers have been investigated. Different starch varieties include high-amylose starch, processed starch such as gelatinized starch and starch ethers and esters may also be used. The innovation requires only granular starch and provides a blend that has physical characteristics very similar to those of the pure polymer. Furthermore, it is claimed that any type of starch is usable, including wheat and rice starch. The capacity to use these inexpensive types of starch greatly enhances the cost efficiency of the invention. With use of granular starch, no additional processing step is needed to prepare plasticized or gelatinized starch. The starch can be from different sources, such as corn, rice, and potato, and can be in either modified or unmodified form. PE can also be of different types, such as linear low-density PE (LDPE) or high-density PE (HDPE). It is also very important to note that the use of starch to replace PE significantly (–15%) reduces production costs.

The patent [6] relates to mixing of starch with a primary polymer and a compatibilizer that has grafted compounds attached to it. These grafting compounds covalently bond to the hydroxyl groups located on granular starch. Starch hydroxyl groups are susceptible to binding by these grafting compounds. Because the starch is chemically grafted to the compatibilizer, which in turn physically interacts with the polymer, the resulting mixture has substantially the same physical properties as the polymer in its pure form. Up to 30% of the mixture may be granular starch. In addition, the starch greatly enhances the biodegradability of the mixture. Polymers with grafting compounds already attached to them are presently commercially available and are only slightly more expensive than the unaltered polymers.

Granule size may vary greatly without significantly affecting the physical properties of the invention. Although granules of approximately 25 micrometers in

diameter are preferred, large variations in granule diameter have only a minimal effect on the physical properties of the end product. Different starches are more plentiful in different parts of the world, so the ability of the invention to utilize a variety of starches is highly advantageous. Starches such as those derived from wheat, corn, rice, and potatoes are only some of the many starches that are suitable.

U.S. Patent No. 6218532 [7] discusses a method of synthesizing materials from amylose starch derivatives. The starch is chemically modified to form starch ethers or esters. No cross-linking of starch to polyethylene occurs. Amylose derivatives with various degrees of substitution and amylose/amylopectin ratios can be used. These chains are chemically cross-linked and are then mechanically stretched to produce a biodegradable and mechanically superior material. Specifically, the process involves starch derivatives such as starch ethers and starch esters. It is claimed that the polymers have degrees of substitution from about 35% to about 95% (degree of substitution is from about 1.05 to about 2.85) and preferably have degrees of substitution from about 1.95 to about 2.70. The starch derivatives are cross-linked to produce permanent entanglements and are processed into sheets, films, fibers, threads, or other articles. After processing, the articles are swollen to the desired volumes in thermodynamically acceptable solvents or solvent mixtures and are deformed in uniaxial or biaxial extensions. The polymer materials are preferably stretched from about 1% to about 500%. Finally, the solvents are removed, yielding homogeneous, highly-ordered materials. The associated increase in van der Waals bonding between the molecules improves the quality of sheets, films, fibers, threads, or other articles with respect to their mechanical properties.

Mixing of starch with a hydrophilic biodegradable polymer—such as polyethylene oxide, for instance—does not need the use of a compatibilizer for covalent attachment of polyethylene to granular starch [8]. For conversion of native starch or starch derivatives into thermoplastic starch, at least one hydrophilic biodegradable polymer has to be added. This hydrophilic biodegradable polymer, which serves as a plasticizer or swelling agent, may be a polymer selected from the following list: an aliphatic polyester, a copolyester with aliphatic and aromatic blocks, a polyester amide, a polyester urethane, a polyethylene oxide polymer and/or a polyglycol, and/or mixtures of these. When the starch, such as in particulate native starch or derivatives thereof, is mixed in the melt with the hydrophilic biodegradable polymer as a plasticizer or swelling agent, to homogenize the mixture, the water content is reduced to <1% by weight based on the weight of the mixture.

Starch polymer can also have polyester grafted onto it [9]. Such a polyester-grafted starch/polymer alloy is capable of imparting practical flexibility and toughness to moldings with no or only a little plasticizer. The polyester-grafted starch/polymer alloy comprises a blend of a polyester-grafted starch (a starch which has polyester graft chains on the starch molecule, with the terminal hydroxyl groups of the polyester graft chains and the hydroxyl groups connected directly to the starch entirely or partly blocked with the ester group) and an independent polyester (a polyester constructed of the same unit as said polyester graft chain, with its

terminal hydroxyl groups entirely or partly blocked with the ester group) which are uniformly mixed together. A method of preparing the alloy and thermoplastic resin compositions containing the alloy are also disclosed.

U.S. Patent No. 5 569 692 [10] describes a starch-based composition for the production of articles of biodegradable plastic materials. The starch is heated with a destructuring agent in order to destructure the starch. It is then mixed with a polymer, preferably polyvinyl alcohol or ethylene vinyl alcohol. This patent does not mention covalent grafting of granular starch onto polyethylene. In order to prepare a starch-based composition usable for the production of articles of biodegradable plastics material, starch is mixed in a heated extruder with a plasticizer with high boiling temperature. A destructuring agent is added for a time sufficient to cause the starch to be destructured. The process temperature should be below the boiling point of the plasticizer and between 120–170 °C. The composition thus obtained is particularly suitable for the formulation of mixtures with polymers of relatively high melting points, because it can be processed at temperatures higher than 120 °C and is suitable for extrusion at low pressure. In particular, compositions thus obtained and mixed with polyvinyl alcohol and/or ethylene vinyl alcohol are suitable for the formation of films by blowing, since they have the desired characteristics of mechanical strength and resistance to tearing and perforation, or for the formation of articles finished by injection molding, thermoforming, or mold blowing.

The most popular method for processing of starch/polymer blends is injection molding for rigid biodegradable products, because of high production rates and accurate product size. During flow, a polymeric material is simultaneously subjected to mechanical and thermal influences, and depending on the morphology, introduces orientation under residual stress. Shrinkage in injection-molded products affects the physical properties and dimensional stabilities of the finished products.

Biodegradable PLS-based multilayer films are useful for packaging or coatings. Multilayer structures present some advantages over blends. Moisture sensitivity is not fully addressed in a blend because of the presence of starchy material close to the surface. Better resistance to moisture in starch-based products can thus be achieved by use of multilayers, allowing the preparation of sandwich-type structures with PLS as the central layer and a hydrophobic component as the surface outer layers. These blends can, for instance, be obtained by different processes – that is, coextrusion, casting, and hot-melt techniques – to protect starch-based materials with waxy layers. Stratified materials can also be obtained by a multistep process based on compression molding. Instances of coating have also been mentioned in the literature. Coating has been achieved by spraying or painting solutions made from biodegradable polyester onto the starch-based material.

Coextrusion seems the best option, because it offers the advantages of being a one-step, continuous, and versatile process [11]. Multilayer coextrusion has been widely used in the past decades to combine the properties of two or more polymers in one single multilayered structure. However, some problems inherent to the multiphasic nature of the flow are likely to occur during coextrusion operations;

these include non-uniform layer distribution, encapsulation, and interfacial instabilities, which are critical because they directly affect the quality and functionality of the multilayer products. Layer encapsulation is essentially the surrounding of the more viscous polymer by the less viscous one. Different stratified structures have been processed by coextrusion and studied: with PCL, PBSA, PEA, PLA, PBAT, or with PHBV. Some research into PLS/PEA/PLS systems has shown that the key parameters are the skin-layer viscosity and thickness, the global extrusion rate, and the die geometry after determination of the stable and unstable flow conditions [6]. The occurrence of instabilities is strongly related to the shear stress at the interface.

2.3

Mechanical Properties of Starch/Polymer Blends

In recent years there has been significant interest in the development of materials from blends of natural and synthetic polymers such as PE or EVOH (ethylene-vinyl-alcohol). To maintain the compostability feature, different biodegradable blends have been developed. These blends can be processed into useful disposable end products with potential to alleviate disposal problems by degrading in selective environments. The mechanical properties of polymer blends depend greatly on the adhesion of the different phases. Poor interfacial adhesion leads to lower ultimate properties, whereas strong interfacial adhesion leads to good mechanical properties and reduced molecular mobility.

There are two fundamental types of transient experiments that can be used to assess viscoelastic properties over time: these are stress relaxation and creep. In the stress relaxation mode, the time decay of stress at a constant strain can be determined; in creep the decrease in strain with constant stress can be investigated. The stress relaxation experiments are useful in predicting the long-term mechanical behavior of materials from short-time experiments.

The primarily studied partially biodegradable starch-based polymer blends are based on polyolefins. Griffin [12] found a biodegradable composition containing a high proportion (over 50%) of biodegradable starch. He proposed a process for making LDPE blown films containing native or modified starch such as thermoplastic starch or plasticized starch and antioxidants such as unsaturated fatty acids and their derivatives. The composition is particularly useful for making trays for meat packaging. These trays are liquid-repellant but gas-permeable.

The mechanical properties and biodegradation of starch/PE blends have been studied extensively. Generally the starch/polyolefin blends are incompatible, and as a result they have larger phase domains than those in a compatible blend. Larger nondegradable residues are therefore produced and can further give rise to secondary pollution in the natural environment. In addition, this incompatibility also leads to poorer mechanical properties. For these reasons, the modification of starch can be advantageous, because smaller domain sizes in the blends can be obtained.

Thakore *et al.* [13] presented results relating to the use of up to 30% of potato starch and stath (starch phthalate) blends with LDPE for injection molding with a comparison of morphologies of specimens by SME microscopy. The rough surface that a starch granule exhibits after esterification provides a site for better adhesion and anchoring, so starch phthalate acts as a better filler than starch. The morphology of a tensile-fractured surface of LDPE shows a uniform continuous matrix. However, the SME pictures of a 70:30 LDPE/starch blend showed voids due to the partial removal of loosely embedded starch granules. This causes phase separation in spite of good dispersion, leading to poor tensile properties for these blends. On the other hand, the morphologies of corresponding LDPE and esterified starch (starch phthalate) blends showed stath particles uniformly distributed and firmly embedded into the LDPE matrix. In addition, the two phases were not easily distinguishable as in the case of LDPE/starch blends. Most of the blends showed lower tensile strength and percentage elongation than LDPE (9.92 MPa and 92.5%, respectively). An increasing percentage of biodegradable component in the blend resulted in decreases both in tensile strength and in elongation at break, although when a proportion of the starch was replaced by stath these properties were both improved. Esterification of starch leads to improvements in its thermoplastic character, thermal stability, hydrophobicity, and crystallinity, so LDPE/stath blends showed better mechanical, thermal, and morphological properties, as well as better biodegradation.

Martin *et al.* [11] reported on the effects of the adhesion strength between the layers on properties of multilayer films. Parameters that affected this adhesion were, among others, polyester type (PCL, PBSA, PEA, PLA, and PHBV) and plasticizer (glycerol) content. The polymers were chosen as the outer layers of the stratified “polyester/plasticized wheat starch/polyester” film structure. The main purpose of the polyester layers was to improve the properties of plasticized wheat starch (PWS) significantly in terms of mechanical performance and moisture resistance. Starchy films (65:35 starch/glycerol ratio) showed elongations at break of 109%, whereas the addition of polyesters increased the elongations at break from 122 to 179% and the tensile strengths from 2.1 for starchy film to 12.3 MPa when polyesters were added. Polyesteramide showed the best adhesion to the PWS layer, which can be attributed to its polar amide groups. PCL and PBSA showed medium adhesion values, and PLA or PHBV were the least compatible polyesters. The same trend in the magnitude of adhesion strength was observed between coextruded and hot-pressed multilayers. It was possible to increase the adhesion properties of the film by up to 50%. This could be achieved by use of polyester blends in the cap layer or PWS/polyester blends in the central layer. Finally, the presence of a polyester cap layer slightly improved the mechanical properties of plasticized starch. These multilayers also have satisfactory water resistance properties [11]. Blending PWS with these polyesters resulted in significant improvements in the properties of plasticized starch, but coating should be preferred.

Walker *et al.* [14] reported on the application of a mechanical process called solid-state shear pulverization (SSSP), creating blends and composites of polyethylene (PE) and damaged starch granules. Starch granules are generally unchanged

when polymer/starch blends are made by melt mixing, and this is the first time that damage (surface roughening, cracking, and clustering) of the starch granule has been reported. The damaging of the starch granule reduces the oxygen permeability. In a 70:30% PE:starch mixture processed by SSSP the permeability was reduced by 29%, in comparison with 21% permeability reduction when melt processing was used and the starch particles were not damaged.

Liu *et al.* [15] tested starch-filled polypropylene (PP) and reported the effect of starch granule size on the crystallization behavior of PP. Differential scanning calorimetry and scanning electron microscopy were used to monitor the changes in energy of crystallization and to characterize the morphologies of PP/starch composites. Little interaction between starch and PP was observed despite the variation in starch granule size. The crystallization temperature of PP decreased with the addition of starch and this decrease became more apparent with increasing starch granule size. The addition of starch also decreased the overall crystallization rate of PP, which can be attributed to an increase in the activation energy of crystallization under nonisothermal conditions. An increase in the size of the starch granules increases the crystallization activation energy of PP and consequently decreases its crystallization rate.

Averous [16] tested biodegradable PLS-based blends that can be useful as fillers in different petroleum polymers. Blending is an easy process by which to obtain materials with improved property/cost performances. This approach is cheaper than the development of new polymers. In addition, blends can be used as models for testing the compatibility between polymeric phases, because a blend presents a large interfacial surface in comparison with, for example, multilayer structures.

Averous *et al.* [17] presented results obtained with different compositions of wheat thermoplastic starch (TPS) and polycaprolactone (PCL) on melt blending by extrusion and injection molding. A large range of blends with different glycerol contents and different starches (wheat starch and PCL) was analyzed. They noted fairly low compatibility between the two polymeric systems, but the addition even of small amounts of PCL to TPS (10%) overcomes the weaknesses of pure TPS: low resilience, high moisture sensitivity, and high shrinkage.

Battachaya [18] processed starch and synthetic polymer blends compounded in a co-rotating extruder. Each blend contained 70% starch, 5% functionalized polymer (HDPEMA, EMA, or EVAMA), and 25% non-functionalized synthetic polymer (high-density polyethylene (HPDE), low-density polyethylene (LDPE), or ethylene vinyl acetate (EVA)). Starch was also blended in amounts of 15%, 30%, 50%, and 60% with synthetic polymer and a compatibilizer was kept constant at a 5% level for all blends. To obtain test samples, all materials were processed by injection molding in the 80–150 °C temperature range. A small amount of maleic anhydride-functionalized synthetic polymers (5% by weight) was added to compatibilize the starch and the synthetic polymer. Starch/HDPE and starch/LDPE blends exhibited stress–strain curves similar to those of ductile polymers, whereas with starch/EVA blends the material was more rubbery. The elastic moduli of starch/HDPE and starch/LDPE blends range between 450 and 550 MPa for the various types of starch (70% starch content), whereas for starch/EVA blends the

elastic moduli ranged from 80 to 110 MPa. As the starch content is increased, the moduli of the blends increase while the elongations at break decrease. Starch/HDPE and starch/LDPE blends showed ductile behavior, whereas starch/EVA blends displayed rubbery characteristics. Blends containing EVA relaxed most rapidly, whereas those containing LDPE took the longest times. The longer relaxation times of LDPE or HDPE blends are probably due to the crystallinities of these synthetic polymers. The slightly longer time required for LDPE melts to relax to a particular reduced stress level could be due to the lower mold temperature (40 °C for LDPE blends as opposed to 45 °C for HDPE blends). In general, as the amylose content in the blend increased, the time taken for the material to relax increased. This is due to the fact that amylose, which is the linear fraction in starch, experiences greater interaction with the anhydride group in the synthetic polymer. Starch/EVA blends showed the fastest relaxation, whereas blends containing LDPE had the slowest.

Blends of recycled LDPE with corn starch have two environmental advantages:

- virgin synthetic thermoplastic material can be substituted by post-consumer materials, and
- the end product can be biodegradable and cheap.

Recycled LDPE/corn starch blends containing 30, 40 and 50 wt% starch were prepared by extrusion [19]. The addition of starch to LDPE reduced the melt flow index values, the tensile strengths, and the elongations at break, whereas the moduli increased. The decreases in the melt flow index and tensile properties were most evident when 40 and 50 wt% starch was added. SEM showed that the interfacial interaction was weak for blends containing virgin and recycled LDPE.

Remkumar *et al.* [20] evaluated the mechanical properties of various compositions of starch/PE blends with addition of EVA (ethylene vinyl acetate), EVAMA (ethylene vinyl acetate maleic anhydride), and EMA (ethylene maleic anhydride), and also with addition of cellulose fibers. The blends were melted in an extruder and were then injection-molded under different conditions. Tensile testing and flexural testing were performed. The corn starch/EMA blends had higher tensile strengths (8.6–11.2 MPa) and were brittle in relation to corn starch/PE blends. Both EMA and PE had comparable elongation and tensile strengths. Blends containing corn starch had higher tensile strengths (9% higher) than wheat starch blends, but elongation of blends containing corn starch was approximately 33% lower. The addition of fibers increased the tensile strength but not the flexural strengths. The mechanical properties of starch/EMA blends were better than those of starch/EVAMA blends.

Park *et al.* [5] presented the first report on blends of potato starch with commonly used plastics such as LDPE and the aliphatic polyester APES (starch/aliphatic polyester, chemical name: poly-(butylene succinate-co-adipate)) with addition of an ionomer. The ionomer used in this study was essentially polyethylene (PE) with a small amount of methacrylic acid copolymerized randomly into the ethylene chain. This was neutralized with Na cation. For each blend, a different level of starch (from 10 to 90% by weight) was used. Measurements of tensile properties

such as tensile strength, elongation at break, and tensile modulus were performed. The biodegradation of the prepared polymer films by microorganisms was investigated in activated compost soil mixtures. Tensile strength values continue to decrease with increasing starch content in starch/LDPE and starch/APES blends. This happens because the hydrophobic LDPE or APES is not compatible with hydrophilic starch. It is a general trend that the better the dispersion of the starch in the thermoplastics matrix, the better are the mechanical properties. In fact, addition of starch generally results in an increase in stiffness. This corresponds to smaller tensile strengths and decreasing elongation at break. For the starch/LDPE and starch/APES blends, the elongation at break and modulus showed the same trend with variation of starch loading. This can be explained by the lack of good phase adhesion, as well as poor dispersion. Park *et al.* [5] also tested the microstructural morphologies of starch/polymer mixtures. It was seen in SEM diagrams that increasing starch loading in starch/LDPE blends decreases the interfacial adhesion and homogeneity. The biodegradation of PE/starch blends suggests that microbes consume starch and create pores in the materials, leading to increases in the surface areas of the PE matrixes and providing susceptible groups for their biodegradation.

Petersen *et al.* [21] reported properties of commercial and semicommercial biobased materials blended with wheat and corn starch and processed by film extrusion, thermoforming, and injection-molding as a basis for primary food packaging and for other uses. The tensile strength and elongation at break showed poorer mechanical properties for the biobased packaging materials than for LDPE and HDPE. The tensile strengths of starchy materials were in the 8 to 20 MPa range, relative to 25 to 50 MPa reached for tested polymers. Wheat and corn starch materials showed water vapor permeabilities three to four times higher than those of the LDPE or HDPE used in the experiments. Use of these materials in combination with edible coatings could improve the water vapor permeability as well as the utilization of films with multiple layers of complementary properties. Furthermore, gas permeability is a limiting factor during food packaging. An increase in the starch content in LDPE-starch blends resulted in higher gas permeabilities, so the biobased materials might be good alternatives for packaging of highly respiring foods.

Processing of wheat starch/polyesteramide blends with addition of glycerol and water were reported by Averous *et al.* [2]. The starch content was kept as the major phase, more than 50%. Mixtures of starch with plasticizers were extruded and granulated, and samples were injection-molded after mixing with polyester. The behavior of pure TPS showed that its tensile strength decreases with increasing glycerol content, whereas the elongation at break increases with higher glycerol content. However, at the highest contents the elongation at break decreases again because of phase separation. The maximum elongation at break was observed when the glycerol/starch ratio was close to 0.2. For brittle materials (10% glycerol content) the addition of polyesteramide resulted in an improvement in impact properties. For more flexible TPS formulations (from 18 to 35% glycerol) the addition of polyesteramide improves all the mechanical characteristics. Addition of

polyesteramide also influences the shrinkage significantly, to provide acceptable values, so this polymer can be considered a dimensional stability enhancer. The polyesteramide did not prevent aging, however, increasing rigidity of the material during the first six weeks was observed. Blending of the starch with polyesteramide was also an efficient way to increase the hydrophobicity. Different combinations of TPS and polyesteramide give a wide range over which mechanical properties could be varied to fit different applications and might represent an interesting approach by which to produce cheaper biodegradable materials.

2.4 Compatibilizers

Environmental threats restrict the use of nondegradable polymers and provide incentive for the development and use of degradable plastics. To obtain a cost-effective biodegradable plastic, starch-filled polyethylene (PE) is still the best alternative, but starch/PE blends are incompatible at the molecular level and often give poor performance. In order to overcome this drawback, either the PE or the starch should be modified. This comparatively new method of producing compatible thermoplastics blends by reactive blending extends to the formation of copolymers or interacting polymers. This differs from other compatibilization methods, which require the addition of separate compatibilizers. In reactive blends, the blend components themselves may be chosen or modified in such a way that reactions occur during melt blending and interfacial adhesion/compatibility of immiscible polymers becomes possible. The small amount of graft polymer formed during the blending and reactions between the components is enough to stabilize the morphology and to improve the blend's properties.

To improve compatibility between two phases, compatibilization strategies are generally developed. This strategy entails the addition of a compound: the compatibilizer, which can be obtained by modification of at least one polymer initially present in the blend. For compatibilization, the following different approaches may be applied [6]:

- the functionalization of the polyester, with maleic anhydride, with pyromellitic anhydride, with polyacrylic acid, or by production of telechelic polyester phosphate;
- the functionalization of starch with polyglycidyl methacrylate, or with urethane functions by treatment with *n*-butylisocyanate;
- starch/polyester reticulation with coupling agents such as peroxides or polyisocyanates;
- the development of copolymers: starch-graft polyester.

The grafting may be achieved by different methods based on the polymers transformed: by the ROP (ring-opening polymerization) technique, for example, or by atom transfer radical polymerization (ATRP). Wide application of these polymerization methods for synthesis of glycopolymer-polypeptide triblock copoly-

mers have been reported by Dong *et al.* [22]. Reactions can be catalyzed with stannous octanoate and initiated with aluminium alkoxides. The length of the grafts can be controlled to obtain a comb structure. The same approaches can be used with PLA-grafted polysaccharides.

The compatibilizer, a commercially available polymer with a grafting compound attached, is mixed with granular starch and the polymer under heat and pressure. The heat and pressure cause the grafting compound in the compatibilizer to bind covalently to hydroxyl groups on the granular starch. The resulting blend has mechanical properties very similar to that of the pure polymer. Furthermore, the reported blend is significantly less expensive than a pure polymer as well as significantly more biodegradable [6]. In the embodiments described below, maleic anhydride is preferred as the grafting compound for the compatibilizer, facilitating covalent bonding of granular starch to the compatibilizer. This is generally because of its ready availability [3].

The compatibilizer improves the mechanical properties of PE/starch, and addition of a plasticizer is actually detrimental to the finished products. Although PE is used here to demonstrate the results of this invention, results are practically the same with other combinations of polymer and compatibilizer as disclosed therein. Incorporation of compatibilizer is easily accomplished by mechanical blending of the polymer, starch, and compatibilizer prior to extrusion. Typically, the compatibilizer is composed of the same polymer as the primary polymer itself. The polymer component of the compatibilizer may be selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-styrene), poly(ethylene terephthalate), polyvinyl fluoride, polyvinyl chloride, or derivatives thereof [6].

Under the heat and pressure conditions used for extruding and curing most hydrophobic polymers an anhydride group will react with a hydroxyl group in order to form a covalent, ester linkage [6]. When a compatibilizer is added to a mixture of starch granules and a hydrophobic polymer, its anhydride groups will react with the hydroxyl groups of the starch granules, causing them to become covalently bound. Typically, the concentration of the compatibilizer is about 10% of that of the starch. However, the amount of compatibilizer may be as much as 80% by weight of the starch.

The starch binding compound is preferably a relatively small percentage of the overall weight of the compatibilizer, typically around 5% [18]. Because of this, large portions of the compatibilizer have no starch binding compound and therefore, no hydrophilicity. These regions of the compatibilizer are very hydrophobic and strongly interact with the polymer in the mixture. A synthetic polymer and starch blend comprises 1–30% starch, 1–24% compatibilizer, and the remainder polymer. The compatibilizer is made up of 75–98% polymer and 2–25% grafting compound, in which grafting compound is covalently attached to the polymer. The compatibilizer should be selected from the group consisting of maleic anhydride or chemicals with similar reactive properties [6]. The resulting mixture is less expensive and more biodegradable than pure polyethylene and has similar mechanical properties, and the mixture absorbs relatively little water.

Maleic anhydride (MA) is an effective starch-binding compound for use in any of a variety of compatibilizers at an amount of 0.01–10 weight % [23]. This is especially so because of the availability of polymers to which maleic anhydride has been grafted. Generally, the polymer component of the compatibilizer should preferably be the same as the polymer being mixed with the starch granules [20]. For example, maleic anhydride-grafted polyethylene (PE-g-MA) is especially suitable for use with PE, both high-density and low-density. Similarly, maleic anhydride grafted polypropylene (PP-g-MA) is especially suitable as a compatibilizer for polypropylene. Both PE-g-MA and PP-g-MA are suitable for use with PET. In addition, it is been found that styrene/ethylene-co-butylene/styrene grafted with maleic anhydride (SEBS-g-MA) is a good compatibilizer for PE, PP, PS, PB, PET, PVC and PVF. For PB, SEBS-g-MA, maleic anhydride grafted polybutylene (PB-g-MA) and glycidyl methyl acrylate grafted polybutylene (PB-g-GMA) are all suitable compatibilizers. In addition, glycidyl methyl acrylate grafted poly(methyl methacrylate) (PMMA-g-GMA) is a good compatibilizer both for PVC and for PVF. Those skilled in the art will appreciate that any polymer that blends well with the polymer being mixed with starch granules should serve well as the polymer compatibilizer.

The European patent registered by Menciloglu and Inceoglu [24], relates to biodegradable thermoplastic nanocomposite materials comprising a melt blend of natural polymer/clay hybrid with polyolefin in the presence of compatibilizer and plasticizer. It presents a method for the preparation of a natural clay nanocomposite and a process for preparing a biodegradable thermoplastic nanocomposite. The combination of polyethylene with the natural polymer and clay in the presented invention increases the processability and melt strength of the natural polymer and the biodegradability of the synthetic polymer and decreases the moisture sensitivity of the biopolymer. The material is superior in mechanical strength, gas barrier properties, biodegradability, processability, and transparency in the presence of plasticizer. The natural polymer component described in this invention may be any natural polymer such as a carbohydrate, keratin, chitosan, cellulose, a protein, or derivatives thereof. It is used in an amount of from 10 to 50 wt%, based on total amount. Derivatives may be modified biopolymers such as acetylated, hydroxypropylated, polyester-grafted, or thermo-plastified starch, carboxymethylated cellulose, or ester-grafted chitosan. Corn starch is preferred because it has the smallest particle size and provides better dispersions in blends with thermoplastic polymer, but starch obtained from wheat, rice, and potato may also be used.

Compatibilizer may be used to provide adhesion between natural polymer/clay hybrid and synthetic polymer. It can be maleic anhydride-grafted polyethylene, glycidyl epoxidized polyethylene, acrylic acid-grafted polyethylene, 3-isopropenyl- α,α -dimethylbenzene isocyanate-grafted (TMI-grafted) polyethylene, or a silane-grafted polyolefin, depending on the biopolymer, and it can be used in an amount of 5 to 30% based on the total weight [24]. Typically, the compatibilizers are incorporated in an amount of 5 to 20 wt%. Suitable plasticizers may be glycerin (glycerol), formamide, ethylene glycol, propylene glycol, polyethylene glycol, sorbitol, or urea and/or may also be a polymer in the form of an aliphatic polyester, a copolyester with aliphatic and aromatic blocks, a polyester amide, a polyester

urethane, a polyethylene oxide polymer, a polyether polyol, polyglycol, and/or mixtures thereof. The plasticizer content can be 25 to 80 wt%, based on the natural polymer. Preferably, the amount of the plasticizer is 25 to 60 wt% [24]. The synthetic resin used may be any thermoplastic material with a melting temperature lower than the degradation temperature of the natural polymer. Polyethylene oxide, low-density polyethylene, high-density polyethylene, polypropylene, and combinations thereof may be chosen as suitable thermoplastic resins. The novel biodegradable nanocomposite materials have relatively rapid biodegradabilities together with excellent mechanical and optical properties, and so are suitable for various applications including the production of agricultural covering mulch films, packaging materials, yoghurt containers, marketing bags, or waste containers for composting. The addition of starch significantly decreases the tensile strength and elongation properties of polyethylene. However when PEgMA was used as a compatibilizer it provided better tensile strengths and elongation values in films, but these were still insufficient for many applications such as packaging bottles etc.

Processes for preparing biodegradable thermoplastic nanocomposite granules comprise the following steps:

- a) dissolution of a natural polymer selected from the group comprising starch, chitosan, carbohydrates, keratin, cellulose, proteins and derivatives thereof such as carboxy-methylated cellulose (CMC), or ester-grafted chitosan, polylactic acid, etc. in a solvent;
- b) adjustment of the pH of the solution to acidic;
- c) addition of 2% to 50 wt% natural clay based on the weight of the natural polymer;
- d) stirring of the solution to obtain a natural polymer/clay nanocomposite precipitate;
- e) melt blending of the natural polymer/clay nanocomposite in an extruder at a suitable temperature of between 110–250 °C with a synthetic polymer selected from the group comprising: polyethylene oxide, low-density polyethylene, high-density polyethylene, polypropylene, and combinations thereof, as well as any polyolefin with a melting temperature lower than the degradation temperature of the natural polymer;
- f) granulation of the material obtained in a pelletizer [24].

Biodegradable thermoplastic nanocomposite polymers obtained by this method are characterized by being transparent and by having improved tensile strengths and good elongation properties.

Yoo *et al.* [25] characterized the interfacial reaction of the polyethylene (PE)/starch blend system containing the reactive compatibilizer maleated polyethylene (m-PE) by FTIR spectroscopy. A significant amount of the anhydride groups on the m-PE existed as their hydrolyzed forms, resulting in a large amount of carboxyl groups. With the aid of a vacuum heating cell designed in the laboratory, the

carboxyl groups were successfully transformed back into the dehydrolyzed state (i.e., anhydride groups). This result enabled the direct spectroscopic observation of chemical reaction occurring at the interface. For the PE/starch blend system containing m-PE, the chemical reaction at the interface was verified by the evolution of ester and carboxyl groups in the FTIR spectra. The effect of the reactive compatibilizer on the interfacial morphology was also examined by scanning electron microscopy (SEM). Enhanced interfacial adhesion was clearly observed for the blend system containing reactive compatibilizer. The tensile strengths of blend systems containing m-PE were also significantly increased in comparison with the corresponding system without compatibilizer. Similar observations were made for the breaking and elongation data.

Corn starch and LDPE (25/100) were pre-mixed with different amounts of compatibilizer (PE-g-MA 0, 5, 10, 15, 20, 25, and 35% w/w based on starch) in order to determine the critical saturated interfacial concentration of PE-g-MA for the corn starch and LDPE system. These mixtures were then melt-blended in a lab-scale twin-screw counter-rotating extruder at 170°C and 50 rpm. When PE-g-MA was added to the blends, the tensile strengths and elongations at break of the blends were improved, and the improvement was more pronounced at higher starch contents. PE-g-MA increased adhesion between the LDPE matrix and the starch filler. The improved interfacial adhesion between LDPE and corn starch had a positive impact on the stress transfer, thus reducing the chance of interfacial de-bonding and leading to improved tensile properties. In addition, these results also supported the conjecture that the interaction between the starch and the PE-g-MA was based on chemistry between the hydroxyl groups in corn starch and the anhydride groups in PE-g-MA, because the polar interaction between them would not improve their properties to any significant extent.

Chandra and Rustgi [26] reported the processing of modified linear low-density polyethylene (LLDPE) blends with starch. Maleic anhydride (MA) was grafted onto LLDPE in xylene in the presence of dicumyl peroxide (DCP) as an initiator. This was needed to bring about some compatibility between starch and synthetic polymers containing polar functional groups that can interact with starch. Corn starch in varying concentrations (between 10 and 60%) was blended with MA-g-LLDPE in a torque rheometer. The same blend compositions of nonfunctional LLDPE with starch were prepared for blends, except in the case of 60% starch content. The tensile strengths and moduli increased and the percentage elongations decreased with increasing starch content in the blends, suggesting interfacial adhesion of the two components of the blend due to reaction. The water absorptions and opacities of the blends also increased with increasing starch content. MA-g-LLDPE/starch blends showed better water resistance than LLDPE/starch blends. Even blends with high starch content (50–60%) could be made significantly water-resistant.

Studies of the biodegradabilities of MA-g-LLDPE/starch blends in soil environment over a period of six months and in mixtures with fungi inoculum for 28 days showed that the samples containing starch contents of more than 30% supported heavy fungus growth and that blends exposed to soil environment degraded more

Table 2.2 Mechanical properties of MA-g-LLDPE/potato starch blends [26].

Blend composition MA-g-LLDPE/starch	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
100/0	13.65	533.49	300.12
90/10	14.36	277.56	342.19
80/20	14.72	237.36	352.22
70/30	14.84	162.36	371.27
60/40	15.01	139.80	417.36
50/50	15.64	124.84	489.21
40/60	16.34	104.27	520.16

than those exposed to fungi alone. This may be because other environmental factors in soil, such as oxygen, humidity, heat, or microorganisms, play synergetic roles and further degrade the samples. The percentages of crystallinity decreased as the starch contents increased, and biodegradation resulted in increases the cristallinity in the tested blends.

Mani and Battachaya [3] also presented results relating to maleic anhydride application to starch/polymer mixtures processed by injection molding. The objective of this work was to study the influence of amylose content on the properties of injection-molded starch/ethylene-vinyl acetate (EVA), starch/ethylene-vinyl acetate maleic anhydride (EVAMA), starch/low-density polyethylene maleic anhydride (EMA) and starch/high-density polyethylene maleic anhydride (HDPEMA) blends. The corn starches used had amylose contents of approximately 0, 25, 50, and 70%. The starch content in the blends was 70% by weight. The properties of injection-molded starch blends with synthetic polymers (ethylene-vinyl acetate, low-density polyethylene, and high-density polyethylene) containing different amounts of amylose and amylopectin in starch were improved by the addition of a small amount (5% by weight) of anhydride-functionalized polymer. The tensile and flexural strengths were increased at an amylose content of 70% and were higher in waxy maize starch (highly branched) blends, presumably due to more crosslinking. In starch/EVA blends, the strength increased with increasing amylose content in the starch, but the values of the mechanical properties for corn starch were much lower than those for potato starch, presented in Table 2.2. Starch blends containing EVA showed greater elongations than blends containing LDPE and HDPE, but lower strengths.

2.5 Conclusions

Many ideas have been proposed for controlling plastics' lifetimes and to accelerate their decomposition to enhance waste reduction. The blending of stable synthetic

polymers with biopolymers and the chemical or physical modification of polymeric composites are examples of solutions used for inducing degradability. Starch is considered a useful material in certain thermoplastic applications because of its biodegradability, availability, non-toxicity, high purity, and low cost. Starch promotes the biodegradability of a non-biodegradable plastic and it can also be used together with a fully biodegradable synthetic polymers, producing biodegradable blends of low costs.

The starch remains in granular form in the plastic matrix and so may act as a filler. On mixing, starch enhances the biodegradability of the synthetic polymer, mainly because of the increase in polymer surface created after consumption of the starch by microorganisms. The mechanical properties are dependent on such factors as filler volume, filler particle size and shape, and the degree of adhesion of the filler to the polymer matrix.

The amount of starch in a blend plays an important role in its biodegradability, as indicated by the soil burial biodegradability test. At present, biopackaging materials are most suitable for foods with high respiration (fruit and vegetables) or for food with short shelf lives (bread, convenience food, etc.), because of poor water barrier properties of these packagings. A main concept for biobased materials applications could be as organic food wrappings in biobased food packaging materials that are environmentally friendly. Additional processing may be needed to improve moisture barrier, by coatings or multilayer coextrusion, for example. It is to be expected that extensive further developments will occur in this field in the near future.

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